GLASS PREPARATION IN SPACE

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ABSTRACT

Low gravity, ease of access to high energy radiation and to high vacuum are conditions making an earth orbiting laboratory unique for developing new glass making processes. Among them are crucible free melting, preparation of glasses sensitive to thermal convection, formation of lenses and mirror blanks with fire polished surface directly from the melt, formation of dispersion filters, ruby glasses and glass-ceramics requiring nucleation control through solid powder dispersion. Advantages of these methods and difficulties to be expected in performing the first experiments will be discussed.

INTRODUCTION

Three experimental conditions existing in an earth orbiting space laboratory call for utilization in glass melting experiments:

(a) Low gravity
(b) Ease of access to high energy radiation
(c) Ease of access to high vacuum

Condition (a) alone or in combination with (b) and/or (c) give an orbiting laboratory its unique features.

Glass melts in high vacuum have been and still are made on a commercial scale in conventional factories chiefly to obtain infrared transmitting glasses. Although it is known that already ultraviolet radiation can change the electronic structure of a glass, e.g., by generating color centers, no experiments have been made up to now to expose glass melts during cooling or rigid glass samples during temperature cycling to such radiation. It should be expected that optical and semiconductive properties of a glass prepared under such conditions or treated in such a manner are different from those of the same glass prepared under normal conditions. However, such experiments can be performed in conventional laboratories, too.

Among the manufacturing processes unique to low gravity environment, as described in general by H. F. Wuenscher [1], the following offer special advantages for glass manufacturing:

(aa) Crucible free melting or remelting

(ab) Melting or remelting of thermal convection sensitive glasses

(ac) Conversion of compacted powders into castings

(ad) Surface tension casting

(ae) Controlled density casting

(af) Nucleation control of crucible free melts through solid powder dispersion

To better understand the significance of these processes as applied to glass melting, a brief review of glass preparation techniques may be given.

GLASS FORMATION FROM MELTS

A glass batch, e.g., of the composition given in table 1, is thoroughly mixed and exposed to a temperature-time relation as shown in Figure 1. Different batches and, in many cases, similar batches melted in different furnaces require different temperature-time curves (see e.g. [2]). To obtain a glass article, the viscous melt is shaped by drawing, blowing, pressing or casting and then quenched. That quenching operation in combination with certain properties of the melt determine the existence of a glass body:

> The cooling rate must be high enough to avoid the formation of crystals in the glass body ("devitrification").
>
> The cooling rate must be low enough to avoid intrinsic fracture of the glass body due to thermal shock.

The numerical values of both limits depend on the composition of the glass, the size and the shape of the body to be produced [4]. For a cylinder of radius b with thermally insulated end faces, the difference Δu between initial temperature of the cylinder and the ambient temperature must fall in the interval

$$(1)\quad \frac{b}{k\cdot h}\cdot\frac{v_m^2}{s_c\cdot|v_m'|}\cdot\frac{1}{g(\tau,\beta)} < \Delta u < \sigma_0\cdot\frac{(1-\mu)}{\alpha\cdot E}\cdot\frac{1}{f(\tau_m,\beta)}\quad ,$$

where

u = temperature
b = cylinder radius
h = heat transfer number
$\beta = (b\cdot h)^{-1}$ = Biot number or modified Nusselt number

} manufacturing parameters

t = time interval during which the center of the cylinder is at a temperature within the devitrification range

t_m = time at which maximum stress occurs in the cylinder surface

$\tau = (k \cdot t)/b^2$ = Fourier modulus

$\tau_m = (k \cdot t_m)/b^2$ = Fourier modulus

} parameters determined by manufacturing conditions and glass properties

k = effective thermal diffusivity

E = Young's modulus

α = coefficient of linear thermal expansion

μ = Poisson's ratio

σ_o = tensile strength

$(v)_m$ = maximum rate of linear crystal growth

v'_m = mean value of (dv/du)

s_c = maximum crystal size allowed for a certain application of the glass — quality parameter

The functions $g(\tau,\beta)$ and $f(\tau_m,\beta)$ are

$$(2) \qquad g(\tau,\beta) = \sum_{\nu=1}^{\infty} \frac{2 \cdot (\beta^2 \cdot \chi_\nu^2)}{\beta \cdot J_o(\chi_\nu) \cdot (1+\beta^2 \chi_\nu^2)} \cdot e^{-\chi_\nu^2 \cdot \tau}$$

$$(3) \qquad f(\tau_m,\beta) = \sum_{\nu=1}^{\infty} \frac{2 \cdot (2\beta^2 - \beta \cdot \chi_\nu)}{\chi_\nu^2 \cdot (1+\beta^2 \cdot \chi_\nu^2)} \cdot e^{-\chi_\nu^2 \cdot \tau_m}$$

χ_ν are the positive roots of the equation

$$(4) \qquad \beta \cdot \chi = J_o(\chi)/J_i(\chi)$$

J_i = Bessel function of order i.

The left hand side of relation (1) is valid in the devitrification range, the right hand side for temperatures below the upper annealing point. A rod of approximately 100 cm length and 8 cm diameter, made of a glass with two different devitrification products (see Figure 2) was slowly cooled violating condition (1). The result is shown in Figure 3.

GLASS MELTING IN ZERO GRAVITY

Crystallization of a piece of glass takes place only if nuclei are present. Many glasses form such nuclei during cooling just because of their chemical composition (homogeneous nucleation). In these cases, zero gravity would not affect devitrification. However, there are glasses in which nuclei are introduced from external sources (heterogeneous nucleation). The most important of these sources is crucible attack by the glass melt. R. P. Olsen mentioned this already in [5]. It can be concluded from his discussion and from the above remarks that glasses may be formed from compounds with even a high rate of crystal growth if they do not exhibit homogeneous (or "intrinsic") nucleation and if they are prepared under conditions which eliminate heterogeneous nucleation. Containerless melting in zero gravity environment and in vacuum is such a process. Since under zero gravity no buoyancy exists for gas bubbles developing during the melting process, the standard glass melting techniques as described (see Figure 1) cannot be applied. Compacted powder of the composition wanted would be one choice for such melting experiments. Batch constituents giving rise to gas evolution during melting must be eliminated. Another problem will be to properly homogenize the melt. Normally, this is done by stirring the viscous glass melt. If heterogeneous nucleation is to be avoided, no mechanical stirring using stirrers made of refractory material is possible. It would have to be investigated if homogenization through rapidly varying force fields is possible. Another possibility would be to raise the temperature of the melt to such a degree that diffusion within the melt compensates concentration gradients. However, increase in temperature would also increase the rate of selective volatilization of glass constituents from

the surface of the melt. Usually this process results in surface devitrification or scum formation. In addition, it must be expected that during the preparation of the powder and the additional pressing, unwanted nuclei are introduced. The most promising starting material would be pure single crystals of sufficient size.

Besides studying the possibilities of developing new glasses in low gravity environment, already existing glasses may have to be melted under such conditions. As an example, the problem of producing laser glasses with extremely high damage threshold may be mentioned. Presently available laser glasses damage due to inclusions at energy density levels of approximately 20 joules/cm^2 (pulse duration 30 nsec). As far as we know today, the damage occurs at inclusions which are either present in the raw glass or developed gradually in a laser glass rod after it has been fired several times. Apparently, ceramic inclusions can be as hazardous as metallic inclusions in this respect. Melting laser glasses of stable composition in volumes of about 10 liters under vacuum and entirely eliminating crucibles may be the only solution to the very serious problem of producing Nd-doped laser glasses with high damage threshold. In this case, surface devitrification would not present a problem since the final laser rod can be prepared from the raw glass billet by optical surfacing and possibly redrawing under conventional conditions.

A number of optical glasses, particularly in the low index/high Abbe number range, are difficult to obtain in large pieces. One reason is their tendency to form striae and even devitrified layers and cords inside the melt. The reason for these defects is not completely understood. There is some indication that thermal gradients in the melt give rise to extreme local variations in the structural equilibrium and, therefore, the physical properties of the melt. Thermal convection in combination with mechanical stirring distributes these structurally different zones over the volume of the melt yielding the above mentioned striation. Elimination of thermal convection and crucible free melting offer the possibility to study the effect of thermal gradients on the optical homogeneity of these glasses. Based on the results of such experiments, the question can

be answered if a process can be developed to produce large pieces of these critical but, for optical designers and laser device engineers, important glasses.

All these experiments would utilize processes of the general nature listed above under (aa), (ab) and (ac).

GLASS FORMING IN ZERO GRAVITY

Surface tension casting, modified by inertia and electric field casting methods, offers the possibility to produce optical elements with fire polished surfaces directly from the melt. Lenses and mirror blanks, usually of rotational symmetry, but in many cases with aspheric surfaces, are presently made by grinding and polishing. Although it is possible to prepare rather smooth surfaces by these methods, there are still irregularities left in the order of 1-10 nm. Firepolished surfaces are smoother by about one order of magnitude. In most optical instruments, the degree of smoothness reached by mechanical polishing is satisfactory. However, there are some special instruments which could be improved in performance if the traces of surface roughness caused by mechanical polishing could be eliminated. Besides selecting small areas out of float glass, there is at present no way to achieve such high quality surfaces under conventional conditions. So-called "precision molding" is applied to produce, e.g., condenser lenses with fire-polished surfaces. In that case, metal or ceramic molds are used to shape the viscous glass at high temperature under various pressures. The reproducibility of the lens' curvature and the elimination of chill wrinkles present real problems. The solution would be to shape the lens without having the hot glass in contact with the mold. Mold-free forming would be limited only by the availability of force fields (inertia and electric) and heat sources in an orbiting laboratory.

Experiments and manufacturing processes related to the preparation of optical elements with fire-polished surfaces directly from glass melts would utilize processes of the general nature listed in the introduction under (ac) and (ad).

PREPARATION OF OPTICAL FILTERS

Glasses containing metallic, semiconductive or dielectric particles are commercially widely used as light filters. Some of them change their effective spectral transmission reversibly while exposed to radiation. Phototropic glasses and a rather unique Cd-S-Se-Te striking glass used as passive Q-switch in ruby laser systems are examples.

"Striking glass", also called "ruby glasses" or "temperature colored glasses", contain colloidally dispersed metallic or semiconductive particles, e.g., such as Au, Ag, Ag-halides, Cd-S compounds, Cd-S-Se compounds, CuO. The spectral transmission of these glasses is determined by the complex refractive index, the shape and the size distribution of these particles if dispersed in a homogeneous glass of the same refractive index. Ruby glasses are presently made on an empirical basis, although it has been shown recently that the spectral transmission of these glasses can be described quantitatively by Mie's scattering theory [6, 7, 8]. Therefore, it should be possible to synthesize ruby glasses with wanted and precalculated spectral transmission by dispersing particles with known optical and electronic properties directly in a glass. At present, these glasses are made utilizing batch reactions which, in most cases, are not fully understood. The glass body formed originally from the melt is almost colorless. A subsequent heat treatment of the colorless sample, involving reactions which are not understood either, yields the final ruby glass. If it would be possible to disperse particles of specific properties in a matrix glass without going through these unknown reactions, completely new types of ruby glasses, e.g., passive Q-switches for Nd or Er lasers or with new phototropic characteristics, could be made. Conversion of compacted powders into castings in zero gravity environment offers such a possibility.

Another example of light filters which could be made in such an environment are the Christiansen filters. They consist of a large number of rather coarse, colorless particles dispersed in a homogeneous, colorless matrix [9]. The optical dispersion curve of the particles and the matrix cross each other at a certain wavelength. At that wavelength,

the mixture is optically homogeneous and light of that wavelength will pass through the mixture undeviated by reflection or refraction at the interface between particles and matrix. The most successful approach to utilize this effect was achieved by McAlister [10]. He packed a cuvette with the particles and filled the remaining space with an appropriate liquid. In a zero gravity environment, Christiansen filters could be prepared in the form of solids by dispersing powder of a high melting glass in a low melting glass matrix. Dispersion curves of some, presently available optical glasses, are shown in Figure 4. Table 2 gives the wavelength of filters which could be obtained by combining pairs of these glasses.

The processes to be utilized in the experiments described in this paragraph would fall under the general categories (ab), (ac), (ae) and (af).

RECOMMENDATIONS FOR EXPERIMENTS

Based on these considerations, a set of experiments should be conducted as shown in Table 3. Preliminary experiments are already carried out in our laboratory with the goal to study the effect of vacuum and different atmospheres on the remelting behavior of several glass types.

After completion of the experiments listed in Table 3, studies should be undertaken to prepare for the manufacturing processes according to Table 4. The same table contains a process which yields a flameproof, thermally insulating lightweight material, namely, foam glass. It might be usable as structural material in or around the space laboratory. Its advantage is mainly that the batch itself weighs only comparatively little. The process is so flexible that the main portion of the batch can utilize material found on the surface of the moon.

References:

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Table 1: Batch composition and analysis expressed in terms of oxides of a glass prepared according to the process described in Fig. 1.

Batch Composition		Oxide Composition	
Constituent	Grams	Constituent	Wt. %
SiO_2	32,889.60	SiO_2	68.52
Na_2CO_3	6,033.60	Na_2O	7.35
K_2CO_3	5,016.00	K_2O	11.13
KNO_3	4,147.20		
$Ba(NO_3)_2$	3,998.40	BaO	4.90
Sb_2O_3	489.60	Sb_2O_3	1.02
$Al(OH)_3$	1,123.20	Al_2O_3	1.53
ZnO	734.40	ZnO	1.53
Li_2CO_3	1,209.60	Li_2O	1.02
Nd_2O_3	1,440.00	Nd_2O_3	3.00
	57,081.60		100.00

Table 2: Approximate values for transmission wavelengths of Christiansen filters (a) and properties of glasses recommended for preparing these filters (b).

(a)

Transmission Wavelength in nm	Matrix Glass	Particles Made of Glass	Thermal Expansion Match
405	SF 15	LaF N3	Good
480	SF 8	LaK 24	Poor
535	SF 8	LaK 3	Good
600	SF 1	LaF N3	Fair
710	SF 15	LaK 24	Poor
780	SF 15	LaK 3	Fair

(b)

Glass Type	Density in cm^3	Transformation Temperature °C	Linear Thermal Expansion Coefficient in $(°C)^{-1} \cdot 10^{-7}$
SF 1	4.46	417	81
SF 8	4.22	423	82
SF 15	4.06	455	79
LaF N3	4.34	620	78
LaK 3	4.35	610	82
LaK 24	3.78	654	59

Table 3: Recommendations for small scale experiments to explore the possibilities of glass manufacturing and glass processing in low gravity environment.

	Experiment - Sample Size: Approximately 5 cm^3	Information to be Obtained
1	Melt tablets of carbonate and nitrate containing batches of optical glasses. 5 different samples; no crucibles; air and vacuum. Total of 10 experiments.	To what an extent can the melts be refined and homogenized in low gravity environment and without stirring?
2	Melt tablets of batches consisting only of oxides. 5 different samples; no crucibles; air and vacuum. Total of 10 experiments.	To what an extent can the melt reactions be completed, the melts be refined and homogenized in low gravity environment and without stirring?
3	Remelt glass spheres with roughly ground surface. 5 different samples; no crucibles; air, forming gas, vacuum. Total of 15 experiments.	What is the quality of firepolished surfaces prepared in vacuum and in low gravity environment?

Table 4: Recommendations for glass manufacturing and glass processing in low gravity environment.

	Process	Product
1	Melt column of batch consisting of high purity raw materials into glass rods.	Laser glass billets (Nd - and Er - doped) of 10-20 liters volume. Dimensions of rods: approximately 8-15 cm diameter; 100-200 cm long.
2	Melt tablets of glass powder mixed with semi-conductive, particularly photoconductive particles in vacuum, nitrogen and air.	Light filters with integral transmission depending on intensity and/or spectral distribution of incident light. Volume of individual samples approximately 100 cm^3.
3	Melt tablets of a low melting glass containing coarse particles of high melting glass.	Christiansen filter. Volume of individual samples approximately 100 cm^3.
4	Remelt optical glass blanks in electric field and/or under rotation.	Lenses and mirror blanks with firepolished surface and non-spherical curves.
5	Remelt blanks of glasses sensitive to thermal convection.	Homogeneous low index-low dispersion glasses in large pieces. Volume of individual blanks approximately 20 liters.
6	Melt foam glass batches.	Structural material to be used in and around the space laboratory.

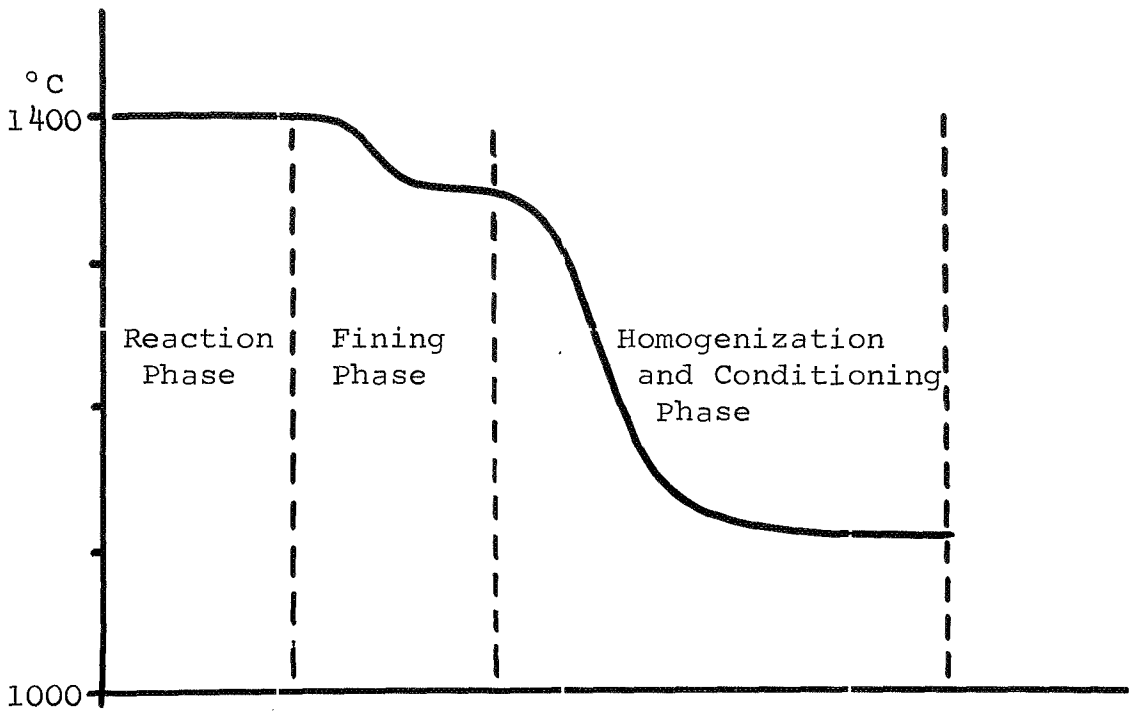

Fig. 1: Temperature-time relation and melting phases of a glass according to Table 1 if prepared in a furnace as described in [3].

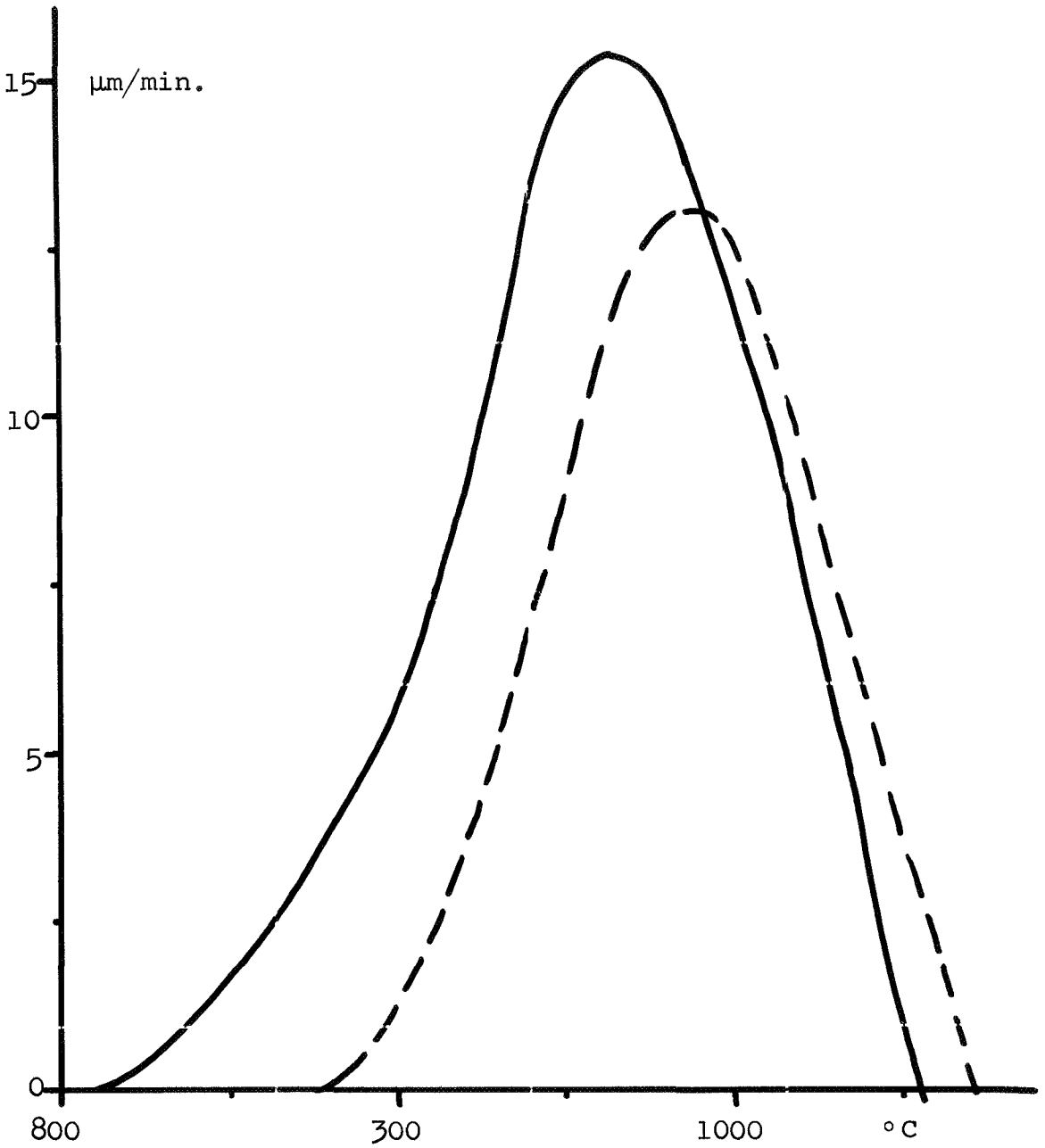

Fig. 2: Rate of linear crystal growth for the two types of devitrification products occurring in a glass of the approximate composition (in weight %):

62 SiO_2, 12 Na_2O, 3 K_2O, 12 CaO, 7 TiO_2, 4 La_2O_3

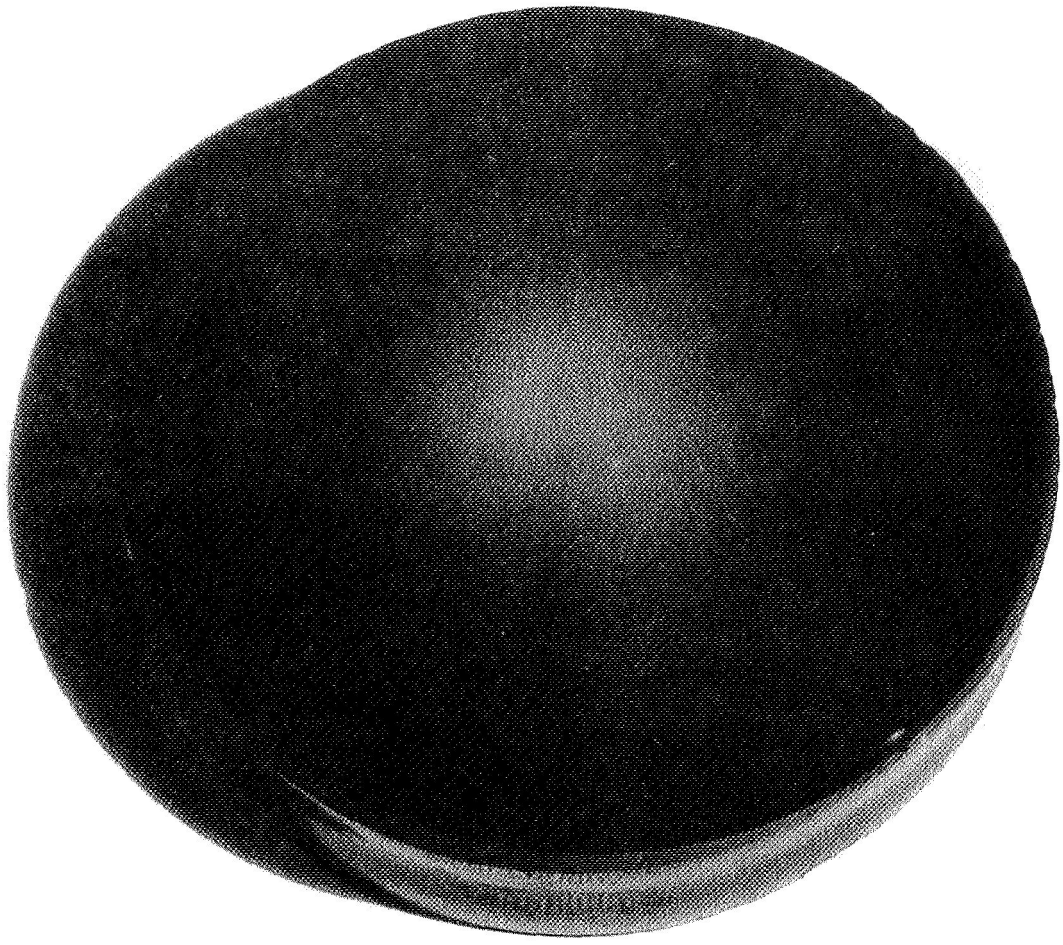

Fig. 3: Cross section through glass cylinder of 7.5 cm diameter quenched under conditions violating relation (1). The bright area in the center of the disc is caused by crystals larger than those in the outer zones.

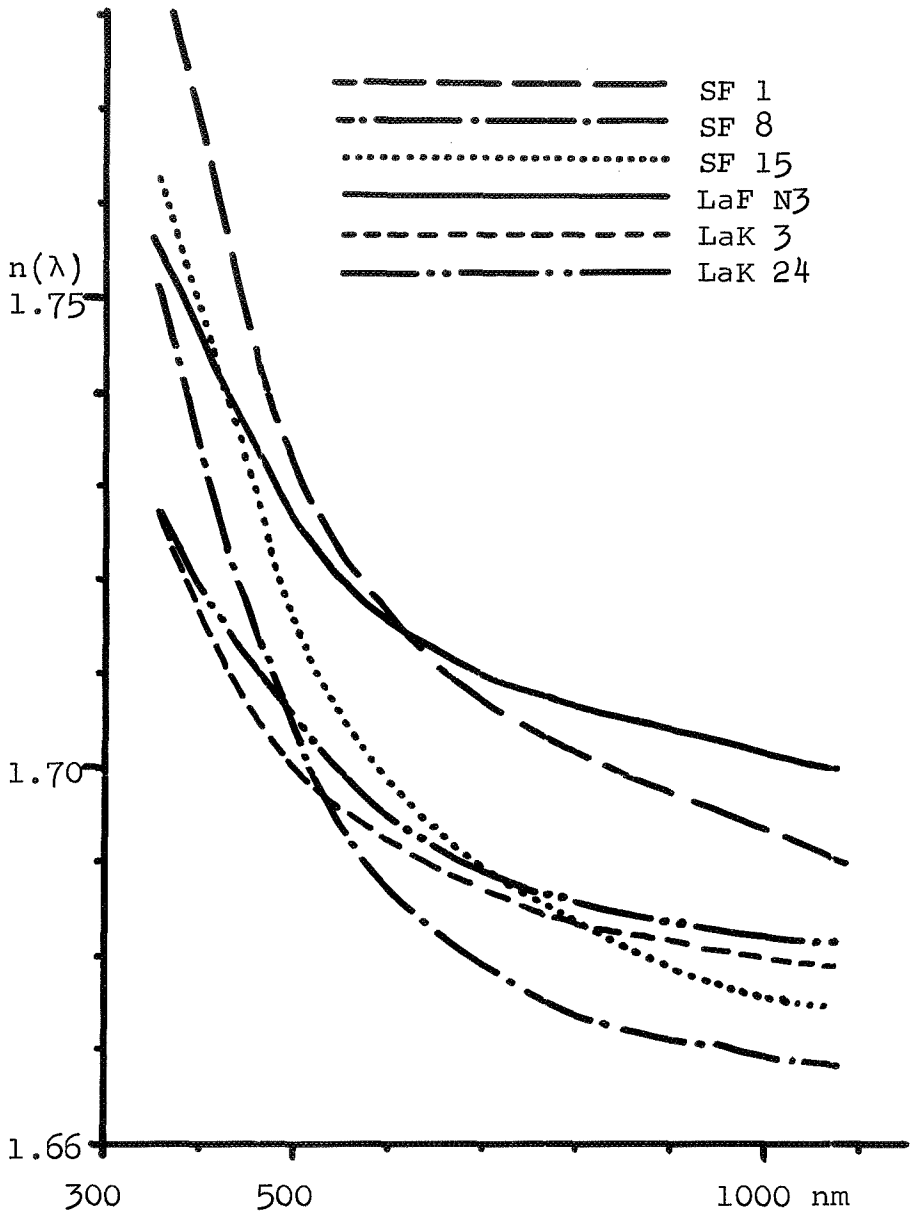

Fig. 4: Dispersion of some optical glasses. Points of intersection of two curves represent the transmission wavelength of a Christiansen filter made by combining the two corresponding glasses.